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(54) Controlling the cross-linking reaction of an aqueous fracturing fluid

(57) In a method for providing controlled delay and improved high temperature gel stability of borated fracturing fluids, a base fluid is first prepared by blending together an aqueous fluid and a hydratable polymer which is capable of gelling in the presence of borate ions. The complexor is prepared by mixing a cross-linking additive capable of furnishing borate ions in solution with a delay additive. The delay additive is effective, within a selected pH range, to chemically bond with both boric acid and the borate ions produced by the cross-linking additive to thereby limit the number of borate ions initially available in solution for subsequent cross-linking of the hydratable polysaccharide. In addition to providing more precise control of the delay time, the complexor provides a reserve of borate which provides improved gel stability at higher temperatures.

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The present invention relates to methods and compositions useful as aqueous well fracturing fluids. It particularly relates to a novel liquid complexor used to obtain controlled delayed gellation of borated polysaccharides and improved gel stability at temperatures above about 200°F.

During hydraulic fracturing, a sand laden fluid is injected into a well bore under high pressure. Once the natural reservoir pressures are exceeded, the fracturing fluid initiates a fracture in the formation which generally continues to grow during pumping. The treatment design generally requires the fluid to reach maximum viscosity as it enters the fracture which affects the fracture length and width. This viscosity is normally obtained by the gellation of suitable polymers, such as a suitable polysaccharide. In recent years, gellation has been achieved by cross-linking these polymers with metal ions including aluminum, antimony, zirconium and titanium containing compounds including the

so-called organotitanates. See, for instance, U.S. Patent No. 4,514,309, issued April 30, 1985, and assigned to the assignee of the present invention.

5 The viscous fracturing fluid being pumped usually encounters high shear in the pipe string during pumping from the surface to the fracture and after entering the fracture, flows at low shear. Recent investigations indicate that the high shear encountered in the pipe string causes extensive degradation of the cross-linked fracturing fluid. Also, 10 high fluid viscosities cause excessive back or friction pressures, limiting the pumping rate, which also affects fracture geometry. These investigations have shown that by delaying the gellation for several minutes during most of the high shear, higher pump rates can be obtained and the 15 fluid generally exhibits better stability.

Recently, guar and guar derivatives cross-linked with borate ions have again become popular. In alkaline water having a pH greater than about 7.8, cross-linking of the guar polymer is essentially instantaneous. This action is 20 probably due to the fact that borates easily and readily esterify with 1,2-cisoidial dialcohols or polyhedral alcohols, such as those found on the guar polymer. This esterification is readily reversible, especially at the elevated temperatures found in the well bore, so that free 25 borate ion is always available. As a result, the delay of borate ion cross-linking systems is difficult to achieve.

Also, for each cross-linking agent, there is a generally recognized maximum temperature where the cross-linker fails to give any increase in viscosity over that 30 observed for the base gel. For boron cross-linked gels,

this upper temperature limit is recognized in the prior art as being between about 150°F to 200°F.

5 Certain of the prior art borated guar systems have employed either slow dissolving metal oxides which slowly increase the fluid alkalinity, which in turn promotes cross-linking, or have used calcium borate salts having poor water solubility, relying upon the slow dissolution of borate ions for delay. In both cases, the delay action was based primarily on the slow dissolution of a solid in the aqueous 10 fracturing fluid, resulting in poor control of the delay time and ultimate viscosity of the fluid. U.S. Patent No. 4,619,776, issued October 28, 1986, to *Mondshine*, is typical of the prior art in teaching the use of a sparingly soluble borate to achieve some degree of control over the cross-linking reaction.

20 *Mondshine* also discusses the use of sparingly soluble borates to achieve some degree of enhanced thermal stability since a "reserve" of boron is available for cross-linking over an extended period of time. However, *Mondshine*'s gel stability examples only extend to an upper temperature limit of 110°C (230°F) and *Mondshine* advises the incorporation of organometallic agents to enhance extreme temperature conditions above 135°C (275°F). The introduction of impurities which are present in the sparingly soluble ores 25 of *Mondshine* can also serve to degrade the overall performance of the fracturing job.

30 In Applicant's previously cited copending application, serial number 07/465,903, there is described a novel chemical mechanism for delaying the cross-linking reaction of a borated fracturing fluid in which the borate ions are

chemically chelated to reduce their initial availability, thus delaying the speed of the cross-linking reaction.

The present invention is directed to the additional discovery that such a chemical chelating mechanism can be used to provide a reserve of borate ions which provides high temperature gel stability for aqueous fracturing fluids at temperatures not previously possible with borated galactomannans.

SUMMARY OF THE INVENTION

The cross-linking system of the invention utilizes a novel complexor solution which both controls the gellation rate of an aqueous fracturing fluid containing a hydrated polysaccharide polymer and provides improved gel stability at temperatures up to about 300°F and above. The complexor solution comprises a cross-linking additive and a delay additive which controls the rate at which the cross-linking additive promotes gellation of the hydrated polymer, the control rate being a function of the pH of the complexor solution. The cross-linking additive is a material which supplies free borate ions in solution and the delay additive is a material which attempts to bind chemically to the borate ions in solution, whereby the hydrated polymer is forced to compete with the delay additive for the free borate ions. Preferably, the delay additive is selected from the group consisting of dialdehydes having about 1 to 4 carbon atoms, keto aldehydes having about 1 to 4 carbon atoms, hydroxyl aldehydes having about 1-4 carbon atoms, ortho substituted aromatic dialdehydes and ortho substituted aromatic hydroxyl aldehydes. The most preferred delay additive is glyoxal.

The cross-linking additive is present in a preselected amount to provide a quantity of borate ions which would be sufficient to normally over-crosslink a base fluid forming a poor quality gel without the presence of the delay additive. The delay additive serves to mask the presence of at least a portion of the borate ions at low temperature, thereby providing a reserve of borate ions for cross-linking the fluid at higher temperatures and providing improved gel stability.

In the method of the invention, a hydratable polymer capable of gelling in the presence of borate ions is blended with an aqueous fluid to form a base fluid and the polymer is allowed to hydrate. A complexor solution is formed for 5 the base fluid by combining a cross-linking additive capable of furnishing borate ions in solution with a delay additive, to chemically bond with both boric acid and the free borate ions produced by the cross-linking additive to thereby limit the number of borate ions available in solution for initial 10 cross-linking of the hydrated polymer. The pH of the complexor solution is adjusted in order to control the rate of the subsequent cross-linking of the hydratable polymer. By properly selecting the amounts of cross-linking additive and delay additive in the complexor solution, a reserve of 15 borate ions is available which are sufficient to cross-link the polymer and to increase the thermal stability of the fracturing fluid at temperatures over 200°F.

Additional objects, features, and advantages will be apparent in the written description which follows.

DETAILED DESCRIPTION OF THE INVENTION

In order to practice the method of the present invention, an aqueous (water or brine) based fracturing fluid is first prepared by blending a hydratable polymer 5 into the base fluid. Any suitable mixing apparatus may be used for this procedure. In the case of batch mixing, the hydratable polymer and aqueous fluid are blended for a period of time which is sufficient to form a hydrated sol. Once the hydration of the polymer is complete, a 10 predetermined quantity of complexor solution is added to the base fluid sufficient to achieve a desired cross-linking reaction time and provide a reserve of borate ions available for cross-linking over a period of time at higher temperatures. The mixture is pumped into the well bore as 15 the cross-linking reaction takes place.

It has been disclosed that the general upper temperature limit for boron cross-linked gels is within the range from about 65°C to about 100°C. By "higher temperatures" is meant temperatures above about 100°C 20 (212°F), at which temperatures desired viscosity increases are not achievable with traditional boron cross-linked fluids.

Propping agents are typically added to the base fluid prior to the addition of the complexor. Propping agents 25 include, for instance, quartz sand grains, glass and ceramic beads, walnut shell fragments, aluminum pellets, nylon pellets, and the like. The propping agents are normally used in concentrations between about 1 to 8 pounds per gallon of fracturing fluid composition, but higher or lower 30 concentrations can be used as required. The base fluid can

also contain other conventional additives common to the well services industry such as surfactants, corrosion inhibitors, buffers, and the like.

5 The hydratable polymer useful in the present invention can be any of the hydratable polysaccharides familiar to those in the well service industry which is capable of gelling in the presence of borate ions to form a gelled base fluid. For instance, suitable hydratable polysaccharides are the galactomannan gums, glucomannan gums, guars, derived 10 guars and cellulose derivatives. Specific examples are guar gum, guar gum derivatives, locust bean gum, karaya gum, carboxymethyl cellulose, carboxymethylhydroxyethyl cellulose, and hydroxyethyl cellulose. The preferred gelling agents are guar gum, hydroxypropyl guar, 15 carboxymethylhydroxypropyl guar, and carboxymethylhydroxyethyl cellulose. A suitable synthetic polymer is polyvinyl alcohol. The most preferred hydratable polymers for the present invention are guar gum and hydroxypropyl guar.

20 The hydratable polymer is added to the aqueous base fluid in concentrations ranging from about 0.10% to 5.0% by weight of the aqueous fluid. The most preferred range for the present invention is about 0.24% to 0.72% by weight.

25 The complexor solution which is used to achieve high temperature gel stability comprises a cross-linking additive and a delay additive which controls the rate at which the cross-linking additive promotes gellation of the hydrated polymer, the control rate being a function of the pH of the complexor solution. The cross-linking additive can be any 30 convenient source of borate ions, for instance the alkali

metal and the alkaline earth metal borates boron monoxide and boric acid. A preferred cross-linking additive is sodium borate decahydrate. The cross-linking additive is present in a preselected amount to provide a quantity of 5 borate ions or boric acid sufficient to normally degrade a base fluid without the presence of its companion delay additive. As will be described, the delay additive serves to mask the presence of at least a portion of the borate ions at low temperature, thereby providing a reserve of 10 borate ions for cross-linking the fluid at higher temperatures and provide improved gel stability. For lower temperature applications, the sodium borate decahydrate is normally present from about 5 to 25 % by weight, most preferably about 10 to 15 % by weight of the complexor 15 solution. For higher temperature applications, the sodium borate decahydrate content will normally be increased, as will be discussed.

The delay additive used in the complexor solution is a material which attempts to bind chemically to the borate 20 ions produced by the cross-linking additive in solution, whereby the hydrated polymer is forced to compete with the delay additive for the borate ions. As will be explained, the effectiveness of the delay additive in chemically bonding to the borate ions in the complexor solution is pH 25 dependent. Thus, unlike the prior art systems which utilized slow dissolving metal oxides or calcium borate salts having poor water solubility, the present complexor does not rely upon the slow dissolution of solids.

Preferably, the delay additive is selected from the 30 group consisting of dialdehydes having about 1-4 carbon atoms, keto aldehydes having about 1-4 carbon atoms, hydroxy

aldehydes having about 1 to 4 carbon atoms, ortho substituted aromatic dialdehydes and ortho substituted aromatic hydroxyl aldehydes. Preferred delay additives include, for instance, glyoxal, propane dialdehyde, 2-keto 5 propanal, 1,4-butanedial, 2-keto butanal, 2,3-butadione, phthaldehyde, salicaldehyde, etc. The preferred delay additive is glyoxal due to its ready availability from a number of commercial sources. Preferably, the delay additive is present in the range from about 5 to 40 % by weight, most 10 preferably about 15 to 30 % by weight of the complexor solution. The preferred ratio of glyoxal to sodium borate ranges from about 1:0.1 to 1:1 at lower temperatures, and can approach 1:0.05 at higher temperatures.

Glyoxal, a 1,2- dialdehyde, hydrates to form 1.1.2.2-tetrahydroxyethane which favorably binds to the borate ions provided by the cross-linking additive of the complexor. As 15 the pH of the complexor solution increases, the rate of gellation declines. As the pH of the complexor solution decreases, the rate of gellation increases. Thus, by 20 adjusting the pH of the complexor solution within a preselected range, extremely accurate control of the cross-linking delay time can be achieved. Experimental delay times have ranged from 10 to 300 seconds by varying the pH 25 of the complexor solution from about 5.0 to 11.50, respectively.

The complexor can also contain a stabilizer which increases the shelf life of the complexor and can serve to enhance the delay time. Suitable stabilizers include, for 30 instance, polyhedric alcohols such as pentaerythritol glycerin, lanolin, mono and oligosaccharides having multiple hydroxyl groups, and the like. The preferred stabilizer is

sorbitol, a reduced sugar. The stabilizer is preferably present in the range from about 5 to 20 % by weight, most preferably about 8 to 10% by weight of the complexor solution.

5 The complexor mixture is prepared by heating to a temperature ranging from ambient to 105°C for 1 to 5 hours. Most preferably heating should range from 65-80°C for 2 to 4 hours.

10 The complexor of the invention can be used to control the delay time of a cross-linked fracturing fluid being pumped into a well bore traversing the subterranean formation to be fractured. The fracturing fluid is pumped at a rate sufficient to fracture the formation and to place propping agents into the fracture. A typical fracturing 15 treatment would be conducted by hydrating a 0.24 to 0.72% galactomannan based polymer, such as a guar, in a 2% (wt/vol) KCl solution at a pH ranging from about 5.0 to 8.5. The pH of the complexor would be adjusted with caustic prior to the treatment to provide the desired delay time. During 20 actual pumping, a buffer would be added to increase the hydrated polymer pH to above 8.0, followed by addition of the complexor, and typically a breaker and proppant. The complexor is preferably added in the range from about 1 to 20 gallons per thousand gallons of fracturing fluid, most 25 preferably in the range from about 2 to 8 gallons per thousand gallons of fracturing fluid. During the treatment, the area close to the well bore will typically begin cooling gradually, resulting in a decreasing gellation rate. The delay time can be easily readjusted to accommodate the 30 cooling by acidifying the complexor.

The following examples of the cross-linked fracturing fluid of the present invention illustrate the controlled delay which can be achieved at lower temperatures and the improved gel stability which can be achieved at higher 5 temperatures. Included are examples of glyoxol/borate formulation, data relating gellation times to complexor pH and gellation stability after cross-linking.

Example 1

Complexor Preparation:

10 Into 300 parts of 40% aqueous glyoxal are added, with stirring, 130 parts of sodium borate decahydrate yielding a milky white suspension. Then, 65 parts of 25% aqueous sodium hydroxide are slowly added resulting in a clear, pale yellow solution. The solution pH can range from 4.90 to 15 6.50. Afterward, 71.4 parts of 70% aqueous sorbitol are added to the solution followed by heating to 95°C for 3 hours. During heating, the solution color changes from pale yellow to amber. After cooling to ambient, the solution pH ranges between 4.50 and 5.00. Each gallon of complexor 20 contains a boron concentration equivalent to 0.29 pounds of elemental boron or 1.65 pounds of boric acid.

Example 2

Gellation Rate:

The base sol used to determine the gellation rate is 25 prepared by adding, with vigorous stirring, 2.4 parts of a 0.4 D.S. hydroxypropyl guar gum and 0.18 parts of sodium bicarbonate to 500 parts of 2% aqueous potassium chloride

solution. After the addition, the stirring rate is reduced to provide mild agitation to the sol for 2 hr. Then, 3.2 parts of 30% aqueous potassium carbonate are added which buffers the sol to about pH 10.0.

5 Meanwhile, the complexor prepared in Example 1 is blended with 0, 4, 8 and 12 parts of 25% aq sodium hydroxide per 100 parts of complexor. The pHs of the treated complexors are shown in Table 1.

10 Then, 250 parts of hydrated sol are transferred to a one liter Waring blender jar and sheared at a rate sufficient to create a vortex exposing the hub nut on the blender blades. Next, 0.98 parts of the treated complexors are added to the sol vortex. The time required for the fluid to viscosify and cover the hub nut is defined as the 15 vortex closure time. These data are also shown in Table 1.

TABLE 1

| | <u>Parts of 25% aq NaOH per 100 parts complexor</u> | <u>Vortex Closure Time (sec.)</u> | <u>Complexor pH</u> |
|----|---|---------------------------------------|-------------------------|
| 20 | 0 | 22 | 4.92 |
| | 4 | 44 | 5.80 |
| | 8 | 121 | 6.09 |
| | 12 | 275 | 8.28 |

Example 3

Shear and thermal stability of borated galactomannans:

The preparation of the base sol used in this example is mixed as described in Example 2. After hydrating for 2 hours, the 500 parts of base sol are treated with 4.5 parts of 30% aqueous potassium carbonate which buffers the sol to 5 about pH 10.3. Afterward, 2.28 parts of complexor containing 0.17 parts of 25% aqueous sodium hydroxide are added to the vigorously stirring sol. After 100 seconds, 42 parts of gel are syringed into a Fann 50C cup. The sample 10 is sheared at 102 sec^{-1} , using an R1B1 cup and bob combination, while heating to 190°F in a preset bath and pressuring to 110 psi with nitrogen. The sample is heated and sheared for 20 minutes followed by a rate sweep using 170, 128, 85 and 42 sec^{-1} while recording stress. These 15 sweeps are repeated about every 30 minutes and the interim rate between sweeps is 102 sec^{-1} . After 359 minutes, the shearing is stopped while heating continues overnight. A final sweep is made after 22 hours and 21 minutes. The rates and stresses are used to calculate the Power Law indices, n' and K , described in the API bulletin RP-39. 20 From the calculated indices, the viscosity of the gel at various shear rates can be calculated and are shown in Table 2 at 170 and 85 sec^{-1} over time.

TABLE 2

| | Time (min) | Temp °F | n' | K lb _m /ft ₂ | Viscosity(cp) 170 s ⁻¹ | Viscosity(cp) 85 s ⁻¹ |
|----|---------------|------------|--------|---------------------------------------|--------------------------------------|-------------------------------------|
| 5 | 20 | 183 | 0.7005 | 0.0497 | 512 | 630 |
| | 51 | 191 | 0.7090 | 0.0420 | 451 | 552 |
| | 81 | 191 | 0.6631 | 0.0456 | 387 | 489 |
| | 112 | 192 | 0.8411 | 0.0144 | 306 | 341 |
| 10 | 141 | 192 | 1.0762 | 0.0040 | 286 | 271 |
| | 172 | 190 | 1.1220 | 0.0028 | 252 | 231 |
| | 202 | 191 | 1.1981 | 0.0016 | 210 | 183 |
| | 232 | 191 | 1.1293 | 0.0020 | 185 | 169 |
| | 262 | 192 | 1.1020 | 0.0022 | 181 | 169 |
| | 292 | 192 | 1.0589 | 0.0025 | 160 | 155 |
| | 359 | 193 | 0.9811 | 0.0020 | 86 | 87 |
| 15 | 1341 | 192 | 0.5486 | 0.0034 | 16 | 20 |

Example 4

Shear and thermal stability of borated galactomannans:

The experiment in Example 3 is repeated using 4.0 parts 30% aqueous potassium carbonate and 1.62 parts of untreated 20 complexor prepared in Example 1. After 60 seconds, 42 parts of gel are syringed into the Fann 50C cup. The fluid is sheared at 102 sec^{-1} while heating to 160°F in a preset bath and pressuring to 110 psi with nitrogen. The rate sweeps are conducted as described in Example 3. After 233 minutes 25 of heating and shearing, the shearing is stopped while heating overnight continues. A final sweep is made after heating for 19 hours and 40 minutes. These data are shown in Table 3.

TABLE 3

| | Time (min) | Temp °F | n' | K lb _m /ft ₂ | Viscosity(cp) 170 s ⁻¹ | Viscosity(cp) 85 s ⁻¹ |
|----|---------------|------------|--------|---------------------------------------|--------------------------------------|-------------------------------------|
| 5 | 20 | 160 | 0.4708 | 0.1844 | 583 | 841 |
| | 51 | 164 | 0.4824 | 0.1530 | 513 | 735 |
| | 80 | 163 | 0.5501 | 0.1038 | 493 | 674 |
| | 111 | 163 | 0.5143 | 0.1143 | 452 | 632 |
| 10 | 141 | 164 | 0.5275 | 0.1047 | 443 | 614 |
| | 171 | 163 | 0.5224 | 0.1044 | 430 | 599 |
| | 203 | 163 | 0.6097 | 0.0625 | 403 | 529 |
| | 233 | 162 | 0.6572 | 0.0419 | 345 | 437 |
| | 1180 | 163 | 0.7992 | 0.0011 | 19 | 21 |

Example 5

Shear and thermal stability of borated galactomannans:

15 The polymer used in Examples 3 and 4 is a hydroxypropyl guar gum. The polymer used in this example is 3.0 parts of a nonderivatized guar gum in 500 parts of 2% aqueous potassium chloride solution mixed as described in Example 2. The sol is stirred for 2 hours prior to adding 4.5 parts of 20 30% aqueous potassium carbonate and 1.12 parts of triethanolamine, a temperature stabilizer. Then with vigorous stirring, 1.30 parts of untreated complexor prepared in Example 1 are added. After 60 seconds of shear, 42 parts of gel are syringed into a Fann 50C cup. The gel 25 is then sheared at 102 sec⁻¹ while heating to 245°F in a preset bath and pressuring to 110 psi with nitrogen. The rate sweeps are routinely made as described in Example 3.

The final sweep is made after shearing and heating for 149 minutes. These data are shown in Table 4.

TABLE 4

| | Time (min) | Temp °F | n' | K lb _m /ft ₂ | Viscosity(cp) 170 s ⁻¹ | Viscosity(cp) 85 s ⁻¹ |
|----|---------------|------------|--------|---------------------------------------|--------------------------------------|-------------------------------------|
| | 20 | 239 | 0.4516 | 0.1763 | 505 | 738 |
| | 50 | 244 | 0.7736 | 0.0298 | 446 | 521 |
| | 83 | 245 | 1.1109 | 0.0046 | 389 | 360 |
| | 119 | 245 | 1.3101 | 0.0008 | 194 | 157 |
| 10 | 149 | 245 | 1.3858 | 0.0003 | 102 | 78 |

The following examples further illustrate the use of the complexor as a high temperature stabilizer. These examples describe three mixtures of the complexor (original) prepared in Example 1 and additional 40% aq glyoxal. The 15 three mixtures are described as per gallon compositions in Table 5. COMPLEXOR A is a 1:1 volume ratio of original complexor and 40% aq glyoxal. COMPLEXOR B is a 1:0.75 volume ratio of complexor to glyoxal and COMPLEXOR C is 1:0.5 volume ratio. In each case, the final COMPLEXOR A, B or C is treated with 25%(wt) caustic solution in a 1(as 20 complexor):0.2(as caustic) volume ratio.

TABLE 5

COMPLEXOR A

(Per Gallon)

25 0.416 gal original complexor from example 1
0.416 gal Glyoxal
0.167 gal 25% NaOH

COMPLEXOR B

(Per Gallon)

5 0.478 gal original complexor from example 1
 0.357 gal Glyoxal
 0.167 gal 25% NaOH

COMPLEXOR C

(Per Gallon)

10 0.555 gal original complexor from example 1
 0.278 gal Glyoxal
 0.167 gal NaOH

The use of approximately using 6 gallons of COMPLEXOR B per thousand gallons of fracturing fluid has been shown to produce a stable gel at 250°F. Six gallons of COMPLEXOR B contains 2.86 gallons of original complexor from Example 1, 15 2.14 gallons of 40% aq glyoxal and 1 gpt 25% (wt) aq NaOH. At this concentration, the boron content is equivalent to 0.82 pounds of elemental boron or 4.72 pounds of boric acid.

20 COMPLEXOR C has been shown to provide more high temperature stability versus time. COMPLEXOR C is used at a concentration of 3 gallons per thousand gallons of aqueous fracturing fluid at 200°F. This concentration of COMPLEXOR C includes 1.725 gallons of original complexor, 0.861 gallons of glyoxal and 0.414 gallons of 25% NaOH. At this concentration, the boron equivalent is 0.49 pounds as 25 elemental boron or 2.85 pounds as boric acid.

Tables 7 and 8 which follow illustrate two different cross-linker loadings and the effect on gel stability. Tables 9 and 10 show the difference in high temperature gel stability achieved by adding extra glyoxal. Tables 11 and

12 illustrate the results achieved with different concentrations of complexor.

TABLE 6

Fluid System: 0.6% (wt/vol) guar gum.
5 Additive: 6 gallons per thousand COMPLEXOR C.

| Time (min) | Temp °F | n' | K lb _m /ft ₂ | Viscosity(cp) at | | |
|---------------|------------|-------|---------------------------------------|---------------------|---------------------|--------------------|
| | | | | 170 s ⁻¹ | 100 s ⁻¹ | 40 s ⁻¹ |
| | 16 | .687 | 22.3455 | 448 | 529 | 704 |
| | 44 | 1.047 | 2.2667 | 289 | 281 | 270 |
| 10 | 73 | .944 | 2.7715 | 208 | 214 | 225 |
| | 101 | .619 | 7.8682 | 111 | 136 | 193 |
| | 129 | .35 | 19.1562 | 68 | 96 | 174 |
| | 158 | .167 | 35.5508 | 49 | 77 | 165 |
| | 186 | .08 | 47.4719 | 42 | 69 | 159 |
| 15 | 214 | .035 | 55.8269 | 39 | 66 | 159 |
| | 243 | .011 | 59.3442 | 37 | 62 | 155 |
| | 271 | .009 | 57.5 | 35 | 60 | 149 |
| | 299 | .008 | 55.6496 | 34 | 58 | 143 |
| | 328 | .008 | 53.5614 | 33 | 56 | 138 |
| 20 | 354 | .009 | 51.1647 | 32 | 53 | 132 |
| | 383 | .014 | 50.1524 | 32 | 53 | 132 |
| | 468 | .003 | 51.3927 | 31 | 52 | 130 |
| | 496 | .017 | 49.1633 | 32 | 53 | 131 |
| | 524 | .009 | 52.1793 | 32 | 54 | 135 |
| 25 | 581 | .005 | 53.0392 | 32 | 54 | 135 |
| | 610 | .006 | 52.2661 | 32 | 54 | 134 |
| | 638 | .014 | 50.7602 | 32 | 54 | 134 |
| | 695 | .026 | 47.1913 | 32 | 53 | 130 |

TABLE 7

Fluid System: 0.54% (wt/vol) guar gum.

Additive: 6.5 gallons per thousand gallons COMPLEXOR B.

| | Time (min) | Temp °F | n' | K lb _m /ft ₂ | Viscosity(cp) at 170 s ⁻¹ | 100 s ⁻¹ | 40 s ⁻¹ |
|----|---------------|------------|-------|---------------------------------------|--|---------------------|--------------------|
| | 2 | 81 | .03 | .2537 | 83 | 139 | 339 |
| | 32 | 249 | .627 | .0758 | 535 | 652 | 917 |
| | 62 | 251 | .651 | .0483 | 385 | 464 | 638 |
| | 93 | 250 | .846 | .0155 | 337 | 366 | 421 |
| 10 | 122 | 249 | 1.029 | .0058 | 325 | 320 | 312 |
| | 152 | 249 | 1.177 | .0024 | 288 | 262 | 223 |
| | 182 | 248 | 1.347 | .0009 | 281 | 234 | 170 |

TABLE 8

Fluid System: 0.54% (wt/vol) guar gum.

15 Additive: 6 gallons per thousand COMPLEXOR B.

| | Time (min) | Temp °F | n' | K lb _m /ft ₂ | Viscosity(cp) at 170 s ⁻¹ | 100 s ⁻¹ | 40 s ⁻¹ |
|----|---------------|------------|------|---------------------------------------|--|---------------------|--------------------|
| | 2 | 88 | .134 | .1554 | 87 | 138 | 305 |
| | 32 | 236 | .362 | .2102 | 380 | 533 | 957 |
| 20 | 62 | 243 | .533 | .1068 | 465 | 596 | 914 |
| | 92 | 248 | .525 | .0994 | 415 | 534 | 825 |
| | 122 | 250 | .64 | .0515 | 388 | 470 | 654 |
| | 152 | 253 | .882 | .0137 | 360 | 384 | 427 |
| | 182 | 253 | .992 | .0076 | 349 | 351 | 354 |

TABLE 9

Fluid System: 0.36% (wt/vol) guar gum.

Additive: 2 gallons per thousand gallons COMPLEXOR C.

| 5 | Time (min) | Temp °F | n' | K lb _m /ft ₂ | Viscosity(cp) at | | |
|----|---------------|------------|------|---------------------------------------|---------------------|---------------------|--------------------|
| | | | | | 170 s ⁻¹ | 100 s ⁻¹ | 40 s ⁻¹ |
| | 2 | 115 | .014 | 1.2342 | 373 | 630 | 1556 |
| | 32 | 190 | .128 | .7384 | 401 | 637 | 1417 |
| | 63 | 194 | .106 | .6006 | 292 | 469 | 1063 |
| | 93 | 196 | .101 | .5466 | 259 | 417 | 950 |
| 10 | 123 | 196 | .109 | .4436 | 219 | 351 | 794 |
| | 153 | 197 | .061 | .478 | 184 | 303 | 717 |
| | 183 | 198 | .028 | .5549 | 180 | 302 | 736 |
| | 213 | 198 | .015 | .6023 | 183 | 309 | 762 |
| | 244 | 199 | .012 | .6277 | 188 | 318 | 785 |
| 15 | 274 | 200 | .009 | .6471 | 191 | 323 | 801 |
| | 304 | 200 | .003 | .6701 | 192 | 325 | 811 |
| | 334 | 200 | .001 | .6747 | 191 | 325 | 811 |
| | 364 | 200 | .001 | .6897 | 195 | 332 | 829 |
| | 395 | 201 | .002 | .6767 | 193 | 327 | 816 |
| 20 | 455 | 201 | .003 | .6871 | 197 | 334 | 832 |
| | 485 | 201 | .002 | .687 | 195 | 332 | 828 |

TABLE 10

Fluid System: 0.36% (wt/vol) guar gum.

Additive: 1.5 gallons per thousand gallons original complexor (Ex. 1).

| | Time (min) | Temp °F | n' | K lb _m /ft ₂ | Viscosity(cp) 170 s ⁻¹ | Viscosity(cp) 100 s ⁻¹ | Viscosity(cp) 85 s ⁻¹ |
|----|---------------|------------|-------|---------------------------------------|--------------------------------------|--------------------------------------|-------------------------------------|
| 5 | 33 | 194 | .492 | 36.3312 | 267 | 350 | 380 |
| | 63 | 191 | .556 | 31.7173 | 324 | 410 | 441 |
| | 94 | 192 | .682 | 17.8267 | 348 | 412 | 434 |
| | 125 | 193 | .691 | 15.9739 | 327 | 385 | 405 |
| | 148 | 194 | .712 | 13.6233 | 310 | 362 | 379 |
| | 178 | 198 | .898 | 5.1232 | 303 | 320 | 326 |
| 10 | 208 | 199 | 1.036 | 2.5288 | 304 | 298 | 297 |
| | 238 | 198 | 1.1 | 1.82 | 304 | 288 | 284 |
| | 268 | 198 | 1.148 | 1.3111 | 280 | 259 | 253 |
| | 298 | 198 | 1.27 | .641 | 256 | 222 | 213 |
| | 329 | 199 | 1.566 | .1212 | 222 | 164 | 150 |
| | 359 | 199 | 1.812 | .0311 | 201 | 131 | 115 |

TABLE 11

Fluid System: 0.36% (wt/vol) guar gum.

Additive: 2.25 gallons per thousand gallons COMPLEXOR C.

| 5 | Time (min) | Temp °F | n' | K lb _m /ft ₂ | Viscosity(cp) at | | |
|----|---------------|------------|-------|---------------------------------------|---------------------|---------------------|--------------------|
| | | | | | 170 s ⁻¹ | 100 s ⁻¹ | 85 s ⁻¹ |
| | 3 | 80 | .386 | .0216 | 44 | 61 | 68 |
| | 33 | 187 | .514 | .0684 | 270 | 350 | 378 |
| | 64 | 192 | .601 | .0501 | 309 | 382 | 408 |
| | 95 | 193 | .594 | .0517 | 308 | 382 | 408 |
| 10 | 121 | 193 | .613 | .0468 | 307 | 377 | 402 |
| | 152 | 194 | .684 | .0332 | 314 | 372 | 391 |
| | 183 | 193 | .733 | .0259 | 315 | 363 | 379 |
| | 213 | 193 | .781 | .0199 | 310 | 348 | 361 |
| | 244 | 194 | .897 | .011 | 312 | 329 | 335 |
| 15 | 275 | 193 | 1.147 | .0031 | 322 | 298 | 291 |

TABLE 12

Fluid System: 0.36% (wt/vol) guar gum.

Additive: 3 gallons per thousand gallons COMPLEXOR C.

| 5 | Time (min) | Temp °F | n' | K lb _m /ft ₂ | Viscosity(cp) at | | |
|----|---------------|------------|------|---------------------------------------|---------------------|---------------------|--------------------|
| | | | | | 170 s ⁻¹ | 100 s ⁻¹ | 40 s ⁻¹ |
| | 16 | 193 | .41 | .186 | 430 | 589 | 1011 |
| | 47 | 194 | .328 | .1807 | 274 | 392 | 725 |
| | 78 | 195 | .496 | .0985 | 354 | 463 | 735 |
| | 109 | 193 | .371 | .1644 | 311 | 435 | 774 |
| 10 | 140 | 194 | .382 | .1492 | 299 | 415 | 731 |
| | 170 | 195 | .421 | .1164 | 285 | 387 | 659 |
| | 201 | 194 | .46 | .1003 | 300 | 400 | 655 |
| | 232 | 194 | .469 | .0978 | 306 | 406 | 661 |
| | 263 | 194 | .461 | .1043 | 314 | 417 | 684 |

TABLE 13

Fluid: 0.6% (wt/vol) guar gum.

Additive: 6 gallons per thousand COMPLEXOR A.

| 5 | Time (min) | Temp °F | n' | K 1b _m /ft ₂ | Viscosity (cp) at | | |
|----|---------------|------------|-------|---------------------------------------|---------------------|---------------------|--------------------|
| | | | | | 170 s ⁻¹ | 100 s ⁻¹ | 40 s ⁻¹ |
| | 20 | 243 | .3181 | .3957 | 571 | 820 | 1532 |
| | 38 | 251 | .3619 | .2814 | 508 | 713 | 1280 |
| | 56 | 265 | .3198 | .3662 | 533 | 765 | 1426 |
| | 85 | 267 | .5028 | .1801 | 671 | 873 | 1377 |
| 10 | 98 | 275 | 1.044 | .0157 | 941 | 919 | 883 |
| | 128 | 277 | 1.263 | .0054 | 1000 | 870 | 684 |
| | 158 | 289 | 1.35 | .0017 | 479 | 397 | 288 |
| | 208 | 290 | 1.3 | .0011 | 249 | 212 | 161 |
| | 243 | 290 | 1.073 | .0022 | 151 | 145 | 136 |
| 15 | 273 | 289 | .89 | .0034 | 93 | 98 | 108 |
| | 303 | 288 | .6667 | .0064 | 55 | 66 | 89 |
| | 333 | 288 | .6582 | .0056 | 47 | 56 | 77 |

An invention has been shown with several advantages. The cross-linking system of the present invention provides an increase in viscosity in an aqueous well fracturing fluid and a stable gelled fluid even at temperatures well above 200°F. The delayed borate cross-linking of the hydrated polymer occurs without the use of suspended solids and does not require the presence of an organometallic adjunct cross-linker to achieve gel stability at temperatures above 200°F. Because the delay mechanism does not rely upon the dissolution of solids in solution, the delay time can be precisely adjusted. The chemical delay mechanism also provides a reserve of borate ions at higher temperatures to improve gel stability.

The complexor of the invention can also be used in a dual cross-link system. Thus, by mixing a traditional borate cross-linker such as boric acid or sodium borate with the complexor, a faster cross-linking time is observed.

5 This effect can be used to enhance the early performance of the system at high temperatures by adding a small amount of either boric acid or sodium borate. This small amount of traditional cross-linker will give extra viscosity to the

10 fluid as it is transporting sand through the tubing string from the well surface. The small increase in viscosity which is observed does not otherwise interfere with the desirable properties of the fluid.

While the invention has been described with respect to its preferred form, it is not thus limited but is

15 susceptible to various changes and modifications without departing from the spirit thereof.

WHAT IS CLAIMED IS:

1. A method of fracturing a subterranean formation comprising the steps of:

5 blending together an aqueous fluid and a hydratable polymer capable of gelling in the presence of borate ions, thereby forming a base fluid;

10 forming a complexor solution for the base fluid by combining a cross-linking additive capable of furnishing borate ions in solution with a delay additive, the delay additive being effective to chemically bond with the borate ions produced by the cross-linking additive to thereby limit the number of borate ions available in solution for subsequent cross-linking of the base fluid;

15 adding the complexor solution to the base fluid to cross-link the fluid; and

chemically masking at least a portion of the borate ions at low temperature while simultaneously providing a reserve of borate ions for cross-linking the fluid at higher temperatures.

2. A method of controlling the cross-linking reaction of an aqueous fracturing fluid in fracturing a subterranean formation, comprising the steps of:

- 5 blending together an aqueous fluid and a hydratable polysaccharide capable of gelling in the presence of borate ions, thereby forming a hydrated polymer sol;
- 10 forming a liquid complexor solution for the hydrated polymer sol by combining a cross-linking additive capable of furnishing borate ions in solution with a delay additive, the delay additive being effective, to chemically bond with both boric acid and the borate ions produced by the cross-linking additive to thereby limit the number of borate ions available in solution for subsequent cross-linking of the hydrated polymer sol;
- 15 adjusting the pH of the complexor solution in order to control the rate of the subsequent cross-linking of the hydrated polymer sol;
- 20 adding the complexor solution to the hydrated polymer sol to cross-link the hydrated polymer sol; and
- 25 wherein the cross-linking additive is present in a preselected amount to provide a quantity of borate ions sufficient to normally over-crosslink a base fluid forming a poor quality gel without the presence of the delay additive, the delay additive serving to mask the presence of at least a portion of the borate ions at low temperature, thereby providing a reserve of borate ions for cross-linking the fluid at higher temperatures and providing improved gel stability.

3. The method of controlling the cross-linking reaction of an aqueous fracturing fluid of claim 2, wherein the hydratable polysaccharide is selected from the group consisting of:

5 guars and derivatized guars, locust bean gum, karaya gum, carboxymethyl cellulose, carboxymethylhydroxyethyl cellulose, hydroxyethyl cellulose, polyvinyl alcohol and mixtures thereof.

10 4. The method of controlling the cross-linking reaction of an aqueous fracturing fluid of claim 3, wherein the cross-linking additive is selected from the group consisting of:

alkali metal borates, alkaline earth metal borates, boric acid boron monoxide and mixtures thereof.

15 5. The method of controlling the cross-linking reaction of an aqueous fracturing fluid of claim 4, wherein said delay additive is selected from the group consisting of:

20 dialdehydes having about 1-4 carbon atoms in the carbon chain, keto aldehydes having about 1-4 carbon atoms in the carbon chain, hydroxyl aldehydes having 1-4 carbon atoms in the carbon chains, ortho substituted aromatic dialdehydes and ortho substituted aromatic hydroxyl aldehydes.

25 6. The method of controlling the cross-linking reaction of an aqueous fracturing fluid of claim 5, wherein the delay additive is glyoxal.

7. A method of fracturing a subterranean formation comprising the steps of:

5 blending together an aqueous fluid and a hydratable polymer capable of gelling in the presence of borate ions, thereby forming a base fluid;

providing a source of borate ions for cross-linking the base fluid at low temperatures;

10 forming a complexor solution for the base fluid by combining a cross-linking additive capable of furnishing borate ions in solution with a delay additive, the delay additive being effective to chemically bond with the borate ions produced by the cross-linking additive to thereby limit the number of borate ions available in solution for subsequent cross-linking of the base fluid;

15 adding the complexor solution to the base fluid to cross-link the fluid; and

20 wherein the cross-linking additive is present in a preselected amount to provide a quantity of borate ions equivalent to at least about 2.50 pounds of boric acid per thousand gallons of base fluid, the delay additive serving to mask the presence of at least a portion of the borate ions at low temperature, thereby providing a reserve of borate ions for cross-linking the fluid at higher temperatures and providing improved gel stability.

8. A method of controlling the cross-linking reaction of an aqueous fracturing fluid in fracturing a subterranean formation, comprising the steps of:

5 blending together an aqueous fluid and a hydratable polysaccharide capable of gelling in the presence of borate ions, thereby forming a hydrated polymer sol;

10 adding an alkaline buffer to thereby adjust the pH of the hydrated polymer sol in the range from about 8.0 to 11.5;

15 forming a complexor solution for said hydrated polymer gel by combining a cross-linking additive capable of furnishing borate ions in solution with a delay additive selected from the group consisting of dialdehydes having about 1-4 carbon atoms in the carbon chain, keto aldehydes having about 1-4 carbon atoms in the carbon chain, hydroxyl aldehydes having 1-4 carbon atoms in the carbon chains, ortho substituted aromatic dialdehydes and ortho substituted aromatic hydroxyl aldehydes, the delay additive being effective, to chemically bond with the borate ions and boric acid produced by the cross-linking additive to thereby limit the number of borate ions available in solution for subsequent cross-linking of the hydrated polymer sol;

20 25 adjusting the pH of the complexor solution to achieve a desired delay in the cross-linking reaction of the hydrated polymer gel, the delay achieved being a function of the complexor solution pH;

adding the complexor solution to the base fluid to cross-link the base fluid; and

wherein the cross-linking additive is present in a preselected amount to provide a quantity of borate ions sufficient to normally over-crosslink a base fluid forming a poor quality gel without the presence of the delay additive,
5 the delay additive serving to mask the presence of at least a portion of the borate ions at low temperature, thereby providing a reserve of borate ions for cross-linking the fluid at higher temperatures, the complexor solution being used in a concentration of about 3 gallons per thousand
10 gallons of base fluid to provide approximately 2.05 pounds of boric acid.

| | | |
|---------------------------|-----|-----------------|
| Relevant Technical fields | | Search Examiner |
| (i) UK CI (Edition | K) | E1F (FPA) |
| (ii) Int CL (Edition | 5) | E21B |
| Databases (see over) | | Date of Search |
| (i) UK Patent Office | | 1 JUNE 1992 |
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Documents considered relevant following a search in respect of claims

1 TO 8

| Category (see over) | Identity of document and relevant passages | Relevant to claim(s) |
|------------------------|--|-------------------------|
| A | US 5082579 (B J SERVICES) | 1,2,7,8 |

| Category | Identity of document and relevant passages | Relevant to claim(s) |
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